

Evaluation of Hylleraas-CI atomic integrals by integration over the coordinates of one electron. IV. An improved algorithm for three-electron kinetic energy integrals.

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Abstract

A method to evaluate the nonrelativistic electron-repulsion, nuclear attraction and kinetic energy three-electron integrals over Slater orbitals appearing in Hylleraas-CI (Hy-CI) electron structure calculations on atoms is shown. It consists on the direct integration over the interelectronic coordinate r_{ij} and the successive integration over the coordinates of one of the electrons. All the integrals are expressed as linear combinations of basic two-electron integrals. These last are solved in terms of auxiliary two-electron integrals which are easy to compute and have high accuracy. The use of auxiliary three-electron ones is avoided, with great saving of storage memory. Therefore this method can be used for Hy-CI calculations on atoms with number of electrons $N \geq 5$. It has been possible to calculate the kinetic energy also in terms of basic two-electron integrals by using the Hamiltonian in Hylleraas coordinates, for this purpose some mathematical aspects like derivatives of the spherical harmonics with respect to the polar angles and recursion relations are treated and some new relations are given.

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1. Introduction

The Hylleraas-Configuration Interaction (Hy-CI) wave functions [2, 3] are of great interest in Quantum Chemistry because they lead to highly accurate energy values, or benchmark calculations, which usually serve to test or calibrate other Quantum Mechanical methods. This possibility of achieving high accuracy has been demonstrated with recent calculations of the helium atom [4], the H_2 molecule [5], the lithium [6], and beryllium atoms [7, 8]. The application of the Hy-CI method can be extended to the calculation of the states of the second period of elements. Hy-CI calculations on the B atom [9] are in progress. Also Hy-CI have been successfully used for the calculation excited states. One example of their applications is the study of atomic excitations during β^- -decay processes of atoms and ions, and the calculation of the final state probabilities [10]. In the future Hy-CI wave functions may be applied to modern problems of Physical Chemistry as confined atoms [11], and Nuclear Physics like the study of excitations during nuclear reactions [12]. Some of these nuclear reactions are important in Nuclear Medicine, like the Boron Neutron Capture Therapy [13], a promising therapy against head and many types of cancer. For all these reasons it is important to provide to future workers in the field with different analytical methods to solve all occurring Hy-CI integrals and to compare their effectiveness in practical calculations.

The kinetic energy integrals, which are generated by the kinetic energy operator part of the Hamiltonian, are not as complex as the repulsion four-electron integrals, but their evaluation is also difficult. Note that the two-electron kinetic-energy integrals are needed not only in computer programs for two-electron systems, but in any program code for larger atoms.

In paper I [14] of this series we have derived analytical expressions for the three-electron kinetic-energy integrals occurring in the Hy-CI method. The Hamiltonian in Hylleraas coordinates was used [15]. The method of derivation consisted in the direct application of the differentiating operators on the wave function. This included to perform derivatives over spherical harmonics and the use of recursion relations over these functions. We distinguished between the cases of one quantum number $m = 0$, $m > 0$, and $m < 0$. In this paper we obtain general expressions for any m quantum number. The most important fact is that the method employed here can be extended in the same fashion to the three-electron case.

The advantage of our method is due to the direct integration over the interelectronic

distances and the coordinates of one of the electrons, reducing the integral to a lower order. The three- and two-electron kinetic energy integrals are reduced to a linear combination of usual two-electron integrals. In appendix A the two-electron integrals are derived in detail.

In the method by Sims and Hagstrom [19] the interelectronic distance is expanded into one-electron distances. The expansion of the interelectronic distances is a concept they use systematically in the evaluation of all kind of integrals. This fact leads to the appearance of three-electron auxiliary integrals W . For contrary using our method for the three-electron kinetic energy integrals no three-electron auxiliary integrals are needed, with a great saving of computer memory. Note that the auxiliary W integrals are three-fold and have to be calculated for a large number of powers and exponents. The number of exponents grows with the atomic number.

We have also checked the two-electron kinetic energy integrals using the Kolos and Roothaan transformation [16], obtaining completely agreement of the integrals to more than 30 decimal digits. Along this work we have used quadruple precision (30 decimal digits in our computer). In appendix B, the Kolos and Roothaan transformation for two-electron kinetic energy integrals is derived. If a similar transformation for the three-electron case can be obtained is still open. The Kolos and Roothaan transformation has shown to be a factor of times computationally faster than the integrals shown here, with identical memory requirements.

The resulting formulas have been programed and used in highly accurate calculations on the ground and excited states of He atom with an accuracy $> 1 \cdot 10^{-10}$ a.u., to obtain some benchmark calculations for the n^1S , $n = 2 - 4$ of the ion Li^+ [10] and in preliminary calculations on the B atom [9]. We shall see that the Kolos and Roothaan transformation provides an effective computational method for the two-electron case. Whereas the integrals and method showed here shall help us to better understanding of the underlying relations in the kinetic energy integrals and it can be used as a method for the three-electron case.

2. The Hylleraas-CI wave function

The Hy-CI wave function [2, 3] is a linear combination of configurations built up with Slater-type atomic orbitals with higher angular momentum as in the regular Configuration-Interaction (CI) procedure and configurations including one interelectronic distance r_{ij} as for

Hylleraas-type trial wave functions [17]. The Hy-CI and CI wave functions for an n -electron systems are defined as:

$$\Psi = \sum_{q=1}^N C_q \Phi_q, \quad \Phi_q = \hat{O}(\hat{L}^2) \hat{\mathcal{A}} \phi_q \chi, \quad (1)$$

where Φ_q are symmetry adapted configurations, N is the number of configurations and the constants C_q are determined variationally. The operator $\hat{O}(\hat{L}^2)$ projects over the proper spatial space, so that every configuration is eigenfunction of the square of the angular momentum operator \hat{L}^2 . $\hat{\mathcal{A}}$ is the n -particle antisymmetrization operator, and χ is the spin eigenfunction:

$$\chi = [(\alpha\beta - \beta\alpha) \dots (\alpha\beta - \beta\alpha) \alpha] \quad (2)$$

where for even electron systems the last α spin function is omitted. The spatial part of the basis functions are Hartree products of Slater orbitals:

$$\phi_q = r_{ij}^\nu \prod_{k=1}^n \phi_k(r_k, \theta_k, \phi_k). \quad (3)$$

The powers ν take the values 0, or 1. For $\nu = 0$ the wave function reduces effectively to a CI wave function. To understand the meaning of the Hy-CI wave function, note that even powers of the interelectronic coordinate are equivalent to products of p -, d -, \dots type one-electron orbitals, for instance:

$$r_{ij}^2 \equiv p(i)p(j). \quad (4)$$

Furthermore, higher odd powers can be expressed as $r_{ij} r_{ij}^{2n}$. It can be demonstrated using the addition theorem of spherical harmonics that a configuration times r_{ij} is equivalent to an infinite expansion of higher angular momentum one-electron orbitals:

$$s(i)s(j)r_{ij} \equiv s(i)s(j) + p(i)p(j) + d(i)d(j) + f(i)f(j) + \dots \quad (5)$$

In this way a single Hy-CI configuration is equivalent to infinite sum of CI configurations containing the excitations of the involved electrons to all higher momentum orbitals.

In this section the two-electron kinetic energy integrals occurring in the Hy-CI method when using the Hamiltonian in Hylleraas coordinates [15] shall be derived. For any atomic number $N \geq 2$ two kinds of kinetic energy integrals occur: two- and three-electron ones. The three-electron kinetic energy integrals can be found in Refs. [14, 19]. In this work we will perform the derivatives directly over r_{ij} and using Hamiltonian written in polar

and interelectronic coordinates, we shall prove its correctness and will solve the resulting integrals in terms of radial two-electron integrals.

Let us define the Slater orbitals specified by the quantum numbers n, m and l with an unnormalized radial part and orthonormal spherical harmonics:

$$\begin{aligned}\phi^*(\mathbf{r}) &= r^{n-1} e^{-\alpha r} Y_l^{m*}(\theta, \phi), \\ \phi'(\mathbf{r}) &= r^{n'-1} e^{-\alpha' r} Y_{l'}^{m'}(\theta, \phi).\end{aligned}\tag{6}$$

The spherical harmonics in Condon and Shortley phases [20, p. 52] are given by:

$$Y_l^m(\theta, \phi) = (-1)^m \left[\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!} \right]^{1/2} P_l^m(\cos \theta) e^{im\phi},\tag{7}$$

with the associated Legendre functions $P_l^m(\cos \theta)$. The spherical harmonics and associated Legendre functions used along this work are written explicitly in [21, p. 14], and defined as in Ref. [?]. They obey the condition:

$$Y_l^{m*}(\theta, \phi) = (-1)^m Y_l^{-m}(\theta, \phi).\tag{8}$$

We define the one-electron charge distributions by expanding or linearizing the products of spherical harmonics with equal argument using the formula [? , Eq. (12)]:

$$Y_l^{m*}(\theta, \phi) Y_{l'}^{m'}(\theta, \phi) = \sum_{L=|l-l'|}^{l+l'} \left[\frac{2L+1}{4\pi} \right]^{1/2} C^L(l', m'; l, m) Y_L^{m'-m}(\theta, \phi),\tag{9}$$

where the Condon-Shortley coefficients [20, Eqs. (6-11)] are defined by:

$$C^L(l', m'; l, m) = \left[\frac{4\pi}{2L+1} \right] \int Y_L^{m'-m}(\theta, \phi) Y_{l'}^{m'*}(\theta, \phi) Y_l^m(\theta, \phi) \sin \theta d\theta d\phi,\tag{10}$$

L_i satisfies the triangular condition $|l_i - l'_i| \leq L \leq l_i + l'_i$ and the restriction $L_i \geq |M_i|$. The summation is done in steps of two: $L_i = |l_i - l'_i|, |l_i - l'_i| + 2, \dots, l_i + l'_i - 2, l_i + l'_i$ and $M_i = m'_i - m_i$. The lowest value of L_i depends also on m_i , for simplicity we will use the notation $|l - l'|$ to recall on l and l' . For discussion about the use of the Condon and Shortley coefficients, see Appendix B and and Appendix in Ref. [?].

The charge distributions are:

$$\Omega_{N,L,M}(\mathbf{r}) = \phi^*(\mathbf{r}) \phi'(\mathbf{r}) = \sum_{L=|l-l'|}^{l+l'} (2L+1)^{1/2} C^L(l', m'; l, m) r^{N-1} e^{-\omega r} Y_L^M(\theta, \phi),\tag{11}$$

where $N = n + n' - 1$, and the exponents $\omega = \alpha + \alpha'$. In the next we will use capital letters N, L, M for the quantum numbers of charge distributions, while low letters n, l, m for the quantum numbers of the orbitals will be used.

The rotation:

Consider the triangle formed by r_1 and r_2 , see Figure 1. The original idea from Calais and Löwdin consisted on making a rotation of one coordinate axis, which allows to make a change of variable in the integral. Letting pass for a moment the z-axis through the r_1 coordinate, the variables are transformed as $\theta_2 \rightarrow \theta_{12}$, and $\phi_2 \rightarrow \phi_{12}$. This may be understood graphically in Figure 1. The volume element of electron 2 may be then written:

$$d\tau_2 = r_2^2 dr_2 \sin \theta_{12} d\theta_{12} d\phi_{12}. \quad (12)$$

As θ_{12} is related to r_{12} through the cosine theorem:

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_{12}, \quad (13)$$

we can differentiate on the left hand side of the equation with respect to r_{12} , and in the other side with respect to θ_{12} :

$$2r_{12} dr_{12} = 2r_1 r_2 \sin \theta_{12} d\theta_{12}, \quad (14)$$

obtaining the relation, which will be used to change the variable of integration:

$$\sin \theta_{12} d\theta_{12} = \frac{r_{12}}{r_1 r_2} dr_{12}. \quad (15)$$

This equation will be used in the direct integration over the variable r_{12} . With the change of integration variable $\theta_{12} \rightarrow r_{12}$, the integration domain changes as $\int_0^\pi \rightarrow \int_{|r_1-r_2|}^{r_1+r_2}$. There are two regions of integration: when $r_1 < r_2$ then $|r_1 - r_2| = r_2 - r_1$ and when $r_2 < r_1$ then $|r_1 - r_2| = r_1 - r_2$. The separation of domains of integration proposed by Perkins [?] has proved to be the best way. Other strategies lead to the same type of formulas. The domain of integration is divided into two parts:

$$J = D_1 - D_2 \quad (16)$$

with:

$$D_1 \rightarrow \int_0^{r_1} dr_2 \int_{r_1-r_2}^{r_1+r_2} dr_{12} + \int_{r_1}^\infty dr_2 \int_{r_1-r_2}^{r_1+r_2} dr_{12} \rightarrow \int_0^\infty dr_2 \int_{r_1-r_2}^{r_2+r_1} dr_{12}, \quad (17)$$

$$D_2 \rightarrow \int_{r_1}^{\infty} dr_2 \int_{r_1-r_2}^{r_1+r_2} dr_{12} - \int_{r_1}^{\infty} dr_2 \int_{r_2-r_1}^{r_1+r_2} dr_{12}. \quad (18)$$

The direct integration over the r_{12} coordinate [?] leads to the separation of the variables r_1 and r_2 :

$$\int_{r_1-r_2}^{r_1+r_2} \frac{1}{2} r_{12}^{\nu} dr_{12} = \frac{1}{(\nu+1)} \sum_{i=1}^{[(\nu+2)/2]} \binom{\nu+1}{2i-1} r_1^{\nu+2-2i} r_2^{2i-1}, \quad (19)$$

where $[(\nu+2)/2]$ is the floor function and denotes the integral part of $(\delta+2)/2$.

The rotation of the axis produces a rotation of the functions, in this case, spherical harmonics. They suffer a transformation given by the rotation matrices, which can be written:

$$Y_{l_2}^{m_2}(\theta_2, \phi_2) = \left(\frac{4\pi}{2l+1} \right)^{1/2} \sum_{m'_2=-l_2}^{l_2} Y_{l_2}^{m_2}(\theta_1, \phi_1) Y_{l_2}^{m'_2}(\theta_{12}, \phi_{12}), \quad (20)$$

For a n -electron system the effective Hamiltonian in Hylleraas coordinates may be written [15]:

$$\begin{aligned} \hat{H} = & -\frac{1}{2} \sum_{i=1}^n \frac{\partial^2}{\partial r_i^2} - \sum_{i=1}^n \frac{1}{r_i} \frac{\partial}{\partial r_i} - \sum_{i=1}^n \frac{Z}{r_i} - \sum_{i<j}^n \frac{\partial^2}{\partial r_{ij}^2} - \sum_{i<j}^n \frac{2}{r_{ij}} \frac{\partial}{\partial r_{ij}} + \sum_{i<j}^n \frac{1}{r_{ij}} \\ & - \frac{1}{2} \sum_{i \neq j}^n \frac{r_i^2 + r_{ij}^2 - r_j^2}{r_i r_{ij}} \frac{\partial^2}{\partial r_i \partial r_{ij}} - \frac{1}{2} \sum_{i \neq j}^n \sum_{k>j}^n \frac{r_{ij}^2 + r_{ik}^2 - r_{jk}^2}{r_{ij} r_{ik}} \frac{\partial^2}{\partial r_{ij} \partial r_{ik}} \\ & - \frac{1}{2} \sum_{i=1}^n \frac{1}{r_i^2} \frac{\partial^2}{\partial \theta_i^2} - \frac{1}{2} \sum_{i=1}^n \frac{1}{r_i^2 \sin^2 \theta_i} \frac{\partial^2}{\partial \varphi_i^2} - \frac{1}{2} \sum_{i=1}^n \frac{\cot \theta_i}{r_i^2} \frac{\partial}{\partial \theta_i} \\ & - \sum_{i \neq j}^n \left(\frac{r_j}{r_i r_{ij}} \frac{\cos \theta_j}{\sin \theta_i} + \frac{1}{2} \cot \theta_i \frac{r_{ij}^2 - r_i^2 - r_j^2}{r_i^2 r_{ij}} \right) \frac{\partial^2}{\partial \theta_i \partial r_{ij}} \\ & - \sum_{i \neq j}^n \frac{r_j}{r_i r_{ij}} \frac{\sin \theta_j}{\sin \theta_i} \sin(\varphi_i - \varphi_j) \frac{\partial^2}{\partial \varphi_i \partial r_{ij}}. \end{aligned} \quad (21)$$

As the Hy-CI wave function consists on only one r_{ij} per configuration and treating now a two electron atom/ion, the terms of the Hamiltonian including $\frac{\partial^2}{\partial r_{12}^2}$ and $\frac{\partial^2}{\partial r_{12} \partial r_{12}}$ vanish.

The angular momentum operator can be extracted:

$$\sum_{i=1}^n \frac{1}{r_i^2} \hat{L}_i^2 = -\frac{1}{2} \sum_{i=1}^n \frac{1}{r_i^2} \frac{\partial^2}{\partial \theta_i^2} - \frac{1}{2} \sum_{i=1}^n \frac{1}{r_i^2 \sin^2 \theta_i} \frac{\partial^2}{\partial \varphi_i^2} - \frac{1}{2} \sum_{i=1}^n \frac{\cot \theta_i}{r_i^2} \frac{\partial}{\partial \theta_i}, \quad (22)$$

and its eigenvalue equation used:

$$\hat{L}_i^2 \phi_i = l_i(l_i + 1) \phi_i, \quad (23)$$

with l_i the angular quantum number of the orbital ϕ_i .

From the variational principle one obtains the matrix eigenvalue problem:

$$(\mathbf{H} - E\mathbf{\Delta})\mathbf{C} = \mathbf{0}, \quad (24)$$

where the matrix elements are:

$$H_{kl} = \int \Phi_k H \Phi_l d\tau, \quad (25)$$

$$\Delta_{kl} = \int \Phi_k \Phi_l d\tau. \quad (26)$$

The Hamiltonian in Hylleraas coordinates can be separated in a sum of one-electron potential and kinetic energy operators.

$$\hat{H} = \sum_{i=1}^n \hat{H}(i), \quad \hat{H}(1) = \hat{T}(1) + \hat{V}(1) = \hat{T}_R(1) + \hat{T}_\theta(1) + \hat{V}(1). \quad (27)$$

The kinetic energy operator can be again separated into radial and angular parts. Let us evaluate the kinetic energy of electron 1 and the interelectronic distance r_{12} :

$$\hat{T}(1) = \hat{T}_{R_1}(1) + \hat{T}_{R_2}(1) + \hat{T}_{R_3}(1) + \hat{T}_L(1) + \hat{T}_{\theta_1}(1) + \hat{T}_{\theta_2}(1) + \hat{T}_{\theta_3}(1). \quad (28)$$

The radial operators are:

$$\hat{T}_{R_1}(1) = -\frac{1}{2} \frac{\partial^2}{\partial r_1^2} - \frac{1}{r_1} \frac{\partial}{\partial r_1}, \quad (29)$$

$$\hat{T}_{R_2}(1) = -\frac{1}{2} \frac{r_1^2 + r_{12}^2 - r_2^2}{r_1 r_{12}} \frac{\partial^2}{\partial r_1 \partial r_{12}}, \quad (30)$$

$$\hat{T}_{R_3}(1) = -\frac{1}{r_{12}} \frac{\partial}{\partial r_{12}}, \quad (31)$$

and the angular ones:

$$\hat{T}_L(1) = \frac{1}{2} \frac{\hat{L}^2(1)}{r_1^2}, \quad \hat{L}^2(1) = -\frac{\partial^2}{\partial \theta_1^2} - \cot \theta_1 \frac{\partial}{\partial \theta_1} - \frac{1}{\sin^2 \theta_1} \frac{\partial^2}{\partial \phi_1^2} \quad (32)$$

$$\hat{T}_{\theta_1}(1) = -\frac{r_2}{r_1 r_{12}} \frac{\cos \theta_2}{\sin \theta_1} \frac{\partial^2}{\partial \theta_1 \partial r_{12}}, \quad (33)$$

$$\hat{T}_{\theta_2}(1) = -\frac{1}{2} \cot \theta_1 \frac{r_{12}^2 - r_1^2 - r_2^2}{r_1^2 r_{12}} \frac{\partial^2}{\partial \theta_1 \partial r_{12}}, \quad (34)$$

$$\hat{T}_{\theta_3}(1) = -\frac{r_2}{r_1 r_{12}} \frac{\sin \theta_2}{\sin \theta_1} \sin(\phi_1 - \phi_2) \frac{\partial^2}{\partial \phi_1 \partial r_{12}}, \quad (35)$$

the potential energy operator is:

$$\hat{V}(1) = -\frac{Z}{r_1}, \quad (36)$$

In the two-electron kinetic energy integrals we may encounter CI configurations $\nu = 0$ and configurations of Hy-CI type with $\nu = 1$. The three-electron integrals J are defined [14]:

$$J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, 1)_{l_1, l'_1, l_2, l'_2, l_3, l'_3}^{m_1, m'_1, m_2, m'_2, m_3, m'_3}$$

are defined in Appendix A, Eq. (A.3) and their value can be calculated using Eqs. (A.12, A.27).

The nuclear attraction potential energy is:

$$\begin{aligned} I_{PE}(1) &= \left\langle \phi(\mathbf{r}_1) \phi(\mathbf{r}_2) \phi(\mathbf{r}_3) r_{13} | \hat{V} | \phi'(\mathbf{r}_1) \phi'(\mathbf{r}_2) \phi'(\mathbf{r}_3) r_{12} \right\rangle \\ &= -Z J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, 1)_{l_1, l'_1, l_2, l'_2, l_3, l'_3}^{m_1, m'_1, m_2, m'_2, m_3, m'_3} \end{aligned} \quad (37)$$

with Z the atomic nuclear charge.

The radial kinetic energy integral is:

$$I_{KE,R}(1) = \left\langle \phi(\mathbf{r}_1) \phi(\mathbf{r}_2) \phi(\mathbf{r}_3) r_{13} | \hat{T}_{R_1}(1) + \hat{T}_{R_2}(1) + \hat{T}_{R_3}(1) | \phi'(\mathbf{r}_1) \phi'(\mathbf{r}_2) \phi'(\mathbf{r}_3) r_{12} \right\rangle \quad (38)$$

The radial part can be separated into three contributions. The resulting integrals can be straightforward evaluated using the operators Eq. (14-16) and the definition of the two-electron integrals Eq. (A.3):

$$I_{KE,R_1}(1) = -\frac{(n_1'^2 + n_1')}{2} J(N_1 - 2, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, 1)_{l_1, l_1', l_2, l_2', l_3, l_3'}^{m_1, m_1', m_2, m_2', m_3, m_3'} \quad (39)$$

$$+ (n_1' \omega_1' + \omega_1') J(N_1 - 1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, 1)_{l_1, l_1', l_2, l_2', l_3, l_3'}^{m_1, m_1', m_2, m_2', m_3, m_3'} \\ - \frac{\omega_1'^2}{2} J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, 1)_{l_1, l_1', l_2, l_2', l_3, l_3'}^{m_1, m_1', m_2, m_2', m_3, m_3'}, \quad (40)$$

$$I_{KE,R_2}(1) = -\frac{(n_1' + 1)}{2} J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; -1, 1)_{l_1, l_1', l_2, l_2', l_3, l_3'}^{m_1, m_1', m_2, m_2', m_3, m_3'} \\ + \frac{\alpha_1'}{2} J(N_1 + 1, N_2, N_3; \omega_1, \omega_2, \omega_3; -1, 1)_{l_1, l_1', l_2, l_2', l_3, l_3'}^{m_1, m_1', m_2, m_2', m_3, m_3'} \\ - \frac{(1 - n_1')}{2} J(N_1 - 2, N_2 + 2, N_3; \omega_1, \omega_2, \omega_3; -1, 1)_{l_1, l_1', l_2, l_2', l_3, l_3'}^{m_1, m_1', m_2, m_2', m_3, m_3'} \\ - \frac{\alpha_1'}{2} J(N_1 - 1, N_2 + 2, N_3; \omega_1, \omega_2, \omega_3; -1, 1)_{l_1, l_1', l_2, l_2', l_3, l_3'}^{m_1, m_1', m_2, m_2', m_3, m_3'} \quad (41)$$

Note the symmetry of these integrals:

$$J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; -1, 1)_{l_1, l_1', l_2, l_2', l_3, l_3'}^{m_1, m_1', m_2, m_2', m_3, m_3'} = J(N_1, N_3, N_2; \omega_1, \omega_3, \omega_2; -1, 1)_{l_1, l_1', l_3, l_3', l_2, l_2'}^{m_1, m_1', m_3, m_3', m_2, m_2'} \quad (42)$$

The last term:

$$I_{KE,R_3}(1) = J(N_1, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, 1)_{l_1, l_1', l_2, l_2', l_3, l_3'}^{m_1, m_1', m_2, m_2', m_3, m_3'}. \quad (43)$$

Now let us evaluate the angular kinetic energy. The integral containing the square of the angular momentum operator can be easily calculated by means of its eigenvalue equation:

$$I_{KE,\theta_1,L} = \left\langle \phi(\mathbf{r}_1) \phi(\mathbf{r}_2) \phi(\mathbf{r}_3) r_{13} \left| \frac{1}{2} \frac{\hat{L}_1^2}{r_1^2} \right| \phi'(\mathbf{r}_1) \phi'(\mathbf{r}_2) \phi'(\mathbf{r}_3) r_{12} \right\rangle \\ = \frac{1}{2} l_1' (l_1' + 1) J(N_1 - 2, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, 1)_{l_1, l_1', l_2, l_2', l_3, l_3'}^{m_1, m_1', m_2, m_2', m_3, m_3'} \quad (44)$$

where l_1' is the quantum number of $\phi(\mathbf{r}_1)$.

The evaluation of the other angular kinetic energy contributions is more involving. The following integrals should be evaluated:

$$I_{KE,\theta_1,1} = - \left\langle \phi(\mathbf{r}_1) \phi(\mathbf{r}_2) \phi(\mathbf{r}_3) r_{13} \left| \frac{r_2}{r_1 r_{12}} \frac{\cos \theta_2}{\sin \theta_1} \frac{\partial^2}{\partial \theta_1 \partial r_{12}} \right| \phi(\mathbf{r}_1) \phi(\mathbf{r}_2) \phi(\mathbf{r}_3) r_{12} \right\rangle, \quad (45)$$

$$I_{KE,\theta_1,2} = -\frac{1}{2} \left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)r_{13} \left| \frac{(r_{12}^2 - r_1^2 - r_2^2)}{r_1^2 r_{12}} \cot \theta_1 \frac{\partial^2}{\partial \theta_1 \partial r_{12}} \right| \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)r_{12} \right\rangle, \quad (46)$$

$$I_{KE,\phi_1,3} = -\left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)r_{13} \left| \frac{r_2}{r_1 r_{12}} \frac{\sin \theta_2}{\sin \theta_1} \sin(\phi_1 - \phi_2) \frac{\partial^2}{\partial \phi_1 \partial r_{12}} \right| \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)r_{12} \right\rangle. \quad (47)$$

3.1 Evaluation of I_{KE,θ_1}

The integral

$$\begin{aligned} I_{KE,\theta_1,1} = & -\left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)r_{13} \left| \frac{r_2}{r_1 r_{12}} \frac{\cos \theta_2}{\sin \theta_1} \frac{\partial^2}{\partial \theta_1 \partial r_{12}} \right| \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)r_{12} \right\rangle = \\ & \frac{1}{(4\pi)^{1/2}} \sum_{L_3=|l_3-l'_3|}^{l_3+l'_3} c_{3L_3} (2L_3+1)^{1/2} \int_0^\infty r_1^{N_1} e^{-\omega_1 r_1} dr_1 \\ & \times \int_0^\infty r_2^{N_2+2} e^{-\omega_2 r_2} r_{12}^{-1} dr_2 \int_0^\infty r_3^{N_3+1} e^{-\omega_3 r_3} r_{13} dr_3 \\ & \times \int_0^\pi \int_0^{2\pi} Y_{L_3}^{M_3}(\theta_3, \phi_3) d\Omega_3 \\ & \times \int_0^\pi \int_0^{2\pi} \cos \theta_2 Y_{l_2}^{m_2*}(\theta_2, \phi_2) Y_{l'_2}^{m'_2}(\theta_2, \phi_2) d\Omega_2 \\ & \times \int_0^\pi \int_0^{2\pi} \frac{1}{\sin \theta_1} Y_{l_1}^{m_1*}(\theta_1, \phi_1) \frac{\partial}{\partial \theta_1} Y_{l'_1}^{m'_1}(\theta_1, \phi_1) d\Omega_1 \quad (48) \end{aligned}$$

with $c_{3L_3} = C^{L_3}(l'_3, m'_3; l_3, m_3)$. $d\Omega_1$ is the volume element $\sin(\theta_1)d\theta_1 d\phi_1$. Let us perform first the angular integration. The derivatives of a spherical harmonic $Y_{l_1}^{m_1}(\theta_1, \phi_1)$ with respect to the polar angle θ_1 [?, 5.7.] is:

$$\frac{\partial Y_{l'_1}^{m'_1}(\theta_1, \phi_1)}{\partial \theta_1} = f_{1a} e^{-i\phi_1} Y_{l'_1}^{m'_1+1}(\theta_1, \phi_1) - f_{1b} e^{i\phi_1} Y_{l'_1}^{m'_1-1}(\theta_1, \phi_1), \quad (49)$$

where:

$$f_{1a} = \frac{1}{2} [(l'_1 + m'_1 + 1)(l'_1 - m'_1)]^{1/2}, \quad f_{1b} = \frac{1}{2} [(l'_1 - m'_1 + 1)(l'_1 + m'_1)]^{1/2} \quad (50)$$

multiplying by the complex conjugate $Y_{l_1}^{m_1*}(\theta_1, \phi_1)$ and linearizing the product using Eq. (A.4) we obtain:

$$Y_{l_1}^{m_1*}(\theta_1, \phi_1) \frac{\partial Y_{l_1'}^{m_1'}(\theta_1, \phi_1)}{\partial \theta_1} = \frac{1}{(4\pi)^{1/2}} \sum_{L_1=|l_1'-l_1|}^{l_1'+l_1} [2L_1+1]^{1/2} \times \{f_{1a}c_{1a}Y_{L_1}^{M_1+1}(\theta_1, \phi_1)e^{-i\phi_1} - f_{1b}c_{1b}Y_{L_1}^{M_1-1}(\theta_1, \phi_1)e^{i\phi_1}\} \quad (51)$$

with

$$c_{1a} = C^{L_1}(l_1', m_1' + 1; l_1, m_1), \quad c_{1b} = C^{L_1}(l_1', m_1' - 1; l_1, m_1). \quad (52)$$

On the other side using the cosine recursion relation:

$$\cos \theta_2 Y_{l_2'}^{m_2'}(\theta_2, \phi_2) = f_{2a} Y_{l_2'-1}^{m_2'}(\theta_2, \phi_2) + f_{2b} Y_{l_2'+1}^{m_2'}(\theta_2, \phi_2), \quad (53)$$

for $l_2' - 1 \geq 0$, otherways the first terms vanishes. The factors are:

$$f_{2a} = \left[\frac{(l_2' + m_2')(l_2' - m_2')}{(2l_2' + 1)(2l_2' - 1)} \right]^{1/2}, \quad f_{2b} = \left[\frac{(l_2' + m_2' + 1)(l_2' - m_2' + 1)}{(2l_2' + 1)(2l_2' + 3)} \right]^{1/2}, \quad (54)$$

multiplying by $Y_{l_2}^{m_2*}(\theta_2, \phi_2)$ and linearizing the products:

$$Y_{l_2}^{m_2*}(\theta_2, \phi_2) \cos \theta_2 Y_{l_2'}^{m_2'}(\theta_2, \phi_2) = \frac{1}{(4\pi)^{1/2}} \sum_{L_2=|l_2'-1-l_2|}^{l_2'-1+l_2} [2L_2+1]^{1/2} f_{2a} c_{2a} Y_{L_2}^{M_2}(\theta_2, \phi_2) + \frac{1}{(4\pi)^{1/2}} \sum_{L_2'=|l_2'+1-l_2|}^{l_2'+1+l_2} [2L_2'+1]^{1/2} f_{2b} c_{2b} Y_{L_2'}^{M_2'}(\theta_2, \phi_2) \quad (55)$$

with

$$c_{2a} = C^{L_2}(l_2' - 1, m_2'; l_2, m_2), \quad c_{2b} = C^{L_2'}(l_2' + 1, m_2'; l_2, m_2).$$

The rotation of $Y_{L_2}^{M_2}(\theta_2, \phi_2)$, see Eq. (A.7), and integration over ϕ_{12} leads to $4\pi Y_{L_2}^{M_2}(\theta_1, \phi_1)$. Altogether (no factor 4π):

$$\begin{aligned}
& -\frac{1}{\sin \theta_1} \left(Y_{l_3}^{m_3*}(\theta_3, \phi_3) Y_{l'_3}^{m'_3}(\theta_3, \phi_3) \right) \left(Y_{l_2}^{m_2*}(\theta_2, \phi_2) \left(\cos \theta_2 Y_{l'_2}^{m'_2}(\theta_2, \phi_2) \right) \right) \\
& \quad \times \left(Y_{l_1}^{m_1*}(\theta_1, \phi_1) \frac{\partial Y_{l'_1}^{m'_1}(\theta_1, \phi_1)}{\partial \theta_1} \right) = \\
& \quad \sum_{L_1=|l'_1-l_1|}^{l'_1+l_1} \sum_{L_3=|l'_3-l_3|}^{l'_3+l_3} [(2L_1+1)(2L_3+1)]^{1/2} \\
& \quad \times c_{3L_3} Y_{L_3}^{M_3}(\theta_3, \phi_3) \left(-\frac{1}{\sin \theta_1} \right) \left\{ \sum_{L_2=|l'_2-1-l_2|}^{l'_2-1+l_2} [2L_2+1]^{1/2} \right. \\
& \quad \left(f_{1a} c_{1a} f_{2a} c_{2a} Y_{L_1}^{M_1+1}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) e^{-i\phi_1} \right. \\
& \quad \left. - f_{1b} c_{1b} f_{2a} c_{2a} Y_{L_1}^{M_1-1}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) e^{i\phi} \right) \\
& \quad + \sum_{L'_2=|l'_2+1-l_2|}^{l'_2+1+l_2} [2L'_2+1]^{1/2} \left(f_{1a} c_{1a} f_{2b} c_{2b} Y_{L_1}^{M_1+1}(\theta_1, \phi_1) Y_{L'_2}^{M_2}(\theta_1, \phi_1) e^{-i\phi_1} \right. \\
& \quad \left. \left. - f_{1b} c_{1b} f_{2b} c_{2b} Y_{L_1}^{M_1-1}(\theta_1, \phi_1) Y_{L'_2}^{M_2}(\theta_1, \phi_1) e^{i\phi_1} \right) \right\} \quad (56)
\end{aligned}$$

Now the spherical harmonics with the same arguments are linearized again, see Eq.(A.4).

$$c_{3L} = C^{L_3}(l'_3, m'_3; l_3, m_3).$$

Note we need the complex conjugate in Eq. (A.10). (easier would be $(-1)^{M_2}$)

$$\begin{aligned}
& (4\pi)^{1/2} (-1)^{M_2} \sum_{L_1=|l'_1-l_1|}^{l'_1+l_1} \sum_{L_3=|l'_3-l_3|}^{l'_3+l_3} [(2L_1+1)(2L_3+1)]^{1/2} c_{3L_3} \left(-\frac{1}{\sin \theta_1} \right) \\
& \quad \times \left\{ \sum_{L_2=|l'_2-1-l_2|}^{l'_2-1+l_2} \sum_{L=|L_2-L_1|}^{L_1+L_2} (-1)^{M_2} [(2L_2+1)(2L+1)]^{1/2} \right. \\
& \quad \left(f_{1a} c_{1a} f_{2a} c_{2a} c_{4a} Y_{L_3}^{M_3}(\theta_1, \phi_1) Y_L^{M_1+M_2+1}(\theta_1, \phi_1) e^{-i\phi_1} \right. \\
& \quad \left. - f_{1b} c_{1b} f_{2a} c_{2a} c_{4b} Y_{L_3}^{M_3}(\theta_1, \phi_1) Y_L^{M_1+M_2-1}(\theta_1, \phi_1) e^{i\phi} \right) \\
& \quad + \sum_{L'_2=|l'_2+1-l_2|}^{l'_2+1+l_2} \sum_{L'=|L'_2-L_1|}^{L_1+L_2} (-1)^{M'_2} [(2L'_2+1)(2L'+1)]^{1/2} \\
& \quad \left(f_{1a} c_{1a} f_{2b} c_{2b} c_{4c} Y_{L_3}^{M_3}(\theta_1, \phi_1) Y_{L'}^{M_1+M_2+1}(\theta_1, \phi_1) e^{-i\phi_1} \right. \\
& \quad \left. \left. - f_{1b} c_{1b} f_{2b} c_{2b} c_{4d} Y_{L_3}^{M_3}(\theta_1, \phi_1) Y_{L'}^{M_1+M_2-1}(\theta_1, \phi_1) e^{i\phi_1} \right) \right\} \quad (57)
\end{aligned}$$

with

$$\begin{aligned} c_{4a} &= C^L(L_1, M_1 + 1; L_2, -M_2), & c_{4b} &= C^L(L_1, M_1 - 1; L_2, -M_2) \\ c_{4c} &= C^{L'}(L_1, M_1 + 1; L'_2, -M_2), & c_{4d} &= C^{L'}(L_1, M_1 - 1; L'_2, -M_2) \end{aligned} \quad (58)$$

$$\begin{aligned} & (4\pi)^{1/2} (-1)^{M_2+M_3} \sum_{L_1=|l'_1-l_1|}^{l'_1+l_1} \sum_{L_3=|l'_3-l_3|}^{l'_3+l_3} [(2L_1+1)(2L_3+1)]^{1/2} c_{3L_3} \left(-\frac{1}{\sin \theta_1} \right) \\ & \times \left\{ \sum_{L_2=|l'_2-1-l_2|}^{l'_2-1+l_2} \sum_{L=|L_2-L_1|}^{L_1+L_2} \sum_{L_4=|L-L_3|}^{L+L_4} (-1)^{M_2+M_3} [(2L_2+1)(2L+1)(2L_4+1)]^{1/2} \right. \\ & \quad \left(f_{1a} c_{1a} f_{2a} c_{2a} c_{4a} c_{5a} Y_{L_4}^{M_1+M_2+M_3+1}(\theta_1, \phi_1) e^{-i\phi_1} \right. \\ & \quad \left. - f_{1b} c_{1b} f_{2a} c_{2a} c_{4b} c_{5b} Y_{L_4}^{M_1+M_2+M_3-1}(\theta_1, \phi_1) e^{i\phi} \right) \\ & + \sum_{L'_2=|l'_2+1-l_2|}^{l'_2+1+l_2} \sum_{L'=|L'_2-L_1|}^{L_1+L_2} \sum_{L'_4=|L'-L_3|}^{L+L'_4} (-1)^{M'_2+M_3} [(2L'_2+1)(2L'+1)(2L'_4+1)]^{1/2} \\ & \quad \left(f_{1a} c_{1a} f_{2b} c_{2b} c_{4c} c_{5c} Y_{L'_4}^{M_1+M_2+M_3+1}(\theta_1, \phi_1) e^{-i\phi_1} \right. \\ & \quad \left. - f_{1b} c_{1b} f_{2b} c_{2b} c_{4d} c_{5d} Y_{L'_4}^{M_1+M_2+M_3-1}(\theta_1, \phi_1) e^{i\phi_1} \right) \left. \right\} \quad (59) \end{aligned}$$

needed are

$$\begin{aligned} c_{5a} &= C^{L_4}(L, M_1 + M_2 + 1; L_3, -M_3), & c_{5b} &= C^{L_4}(L, M_1 + M_2 - 1; L_3, -M_3) \\ c_{5c} &= C^{L'_4}(L', M_1 + M_2 + 1; L_3, -M_3), & c_{5d} &= C^{L'_4}(L', M_1 + M_2 - 1; L_3, -M_3) \end{aligned} \quad (60)$$

Finally, the recursion relation containing the sine function is applied [14, C7]:

$$\begin{aligned} -\frac{Y_l^m(\theta_1, \phi_1)}{\sin \theta_1} &= \frac{1}{2m} \left[\frac{(2l+1)}{(2l+3)} \right]^{1/2} [(l-m+2)(l-m+1)]^{1/2} e^{i\phi_1} Y_{l+1}^{m-1}(\theta_1, \phi_1) \\ &+ ((l+m+1)(l+m+2))^{1/2} e^{-i\phi_1} Y_{l+1}^{m+1}(\theta_1, \phi_1), \end{aligned} \quad (61)$$

The relation is valid for $m \neq 0$. This condition is fulfilled in our cases $M = M_1 + M_2 + M_3 + 1$ and $M' = M_1 + M_2 + M_3 - 1$. Multiplying $1/\sin \theta_1$ and Eq. (40) we have:

$$\begin{aligned}
I_{KE,\theta_1}(1) &= (4\pi)^{1/2}(-1)^{M_2+M_3} \sum_{L_1=|l'_1-l_1|}^{l'_1+l_1} \sum_{L_3=|l'_3-l_3|}^{l'_3+l_3} [(2L_1+1)(2L_3+1)]^{1/2} c_{3L_3} \\
&\quad \left\{ \sum_{L_2=|l'_2-1-l_2|}^{l'_2-1+l_2} \sum_{L=|L_2-L_1|}^{L_1+L_2} \sum_{L_4=|L-L_3|}^{L+L_4} (-1)^{M_2+M_3} (2L+1) \left[\frac{(2L_2+1)(2L_4+1)}{(2L+3)} \right]^{1/2} \right. \\
&\quad \left(f_{1a}c_{1a}f_{2a}c_{2a}f_{3a}c_{4a}c_{5a} \int_0^\pi \int_0^{2\pi} Y_{L+1}^{M_1+M_2+M_3}(\theta_1, \phi_1) d\Omega_1 \right. \\
&\quad + f_{1a}c_{1a}f_{2a}c_{2a}f_{3b}c_{4a}c_{5a} \int_0^\pi \int_0^{2\pi} Y_{L+1}^{M_1+M_2+M_3+2}(\theta_1, \phi_1) e^{-2i\phi_1} d\Omega_1 \\
&\quad - f_{1b}c_{1b}f_{2a}c_{2a}f_{3a}c_{4b}c_{5b} \int_0^\pi \int_0^{2\pi} Y_{L+1}^{M_1+M_2+M_3-2}(\theta_1, \phi_1) e^{2i\phi} d\Omega_1 \\
&\quad \left. \left. - f_{1b}c_{1b}f_{2a}c_{2a}f_{3b}c_{4b}c_{5b} \int_0^\pi \int_0^{2\pi} Y_{L+1}^{M_1+M_2+M_3}(\theta_1, \phi_1) d\Omega_1 \right) \right. \\
&\quad \times J(N_1-1, N_2+1, N_3; \omega_1, \omega_2, \omega_3; -1, 1; L_2, L_3) \\
&+ \sum_{L'_2=|l'_2+1-l_2|}^{l'_2+1+l_2} \sum_{L'=|L'_2-L_1|}^{L_1+L_2} (-1)^{M'_2+M_3} (2L'+1) \left[\frac{(2L_2+1)(2L'_4+1)}{(2L+3)} \right]^{1/2} \\
&\quad \left(f_{1a}c_{1a}f_{2b}c_{2b}f_{3c}c_{4c}c_{5c} \int_0^\pi \int_0^{2\pi} Y_{L'+1}^{M_1+M_2+M_3}(\theta_1, \phi_1) d\Omega_1 \right. \\
&\quad + f_{1a}c_{1a}f_{2b}c_{2b}f_{3d}c_{4c}c_{5c} \int_0^\pi \int_0^{2\pi} Y_{L'+1}^{M_1+M_2+M_3+2}(\theta_1, \phi_1) e^{-2i\phi_1} d\Omega_1 \\
&\quad - f_{1b}c_{1b}f_{2b}c_{2b}f_{3c}c_{4d}c_{5d} \int_0^\pi \int_0^{2\pi} Y_{L'+1}^{M_1+M_2+M_3-2}(\theta_1, \phi_1) e^{2i\phi_1} d\Omega_1 \\
&\quad \left. \left. - f_{1b}c_{1b}f_{2b}c_{2b}f_{3d}c_{4d}c_{5d} \int_0^\pi \int_0^{2\pi} Y_{L'+1}^{M_1+M_2+M_3}(\theta_1, \phi_1) d\Omega_1 \right) \right. \\
&\quad \times J(N_1-1, N_2+1, N_3; \omega_1, \omega_2, \omega_3; -1, 1; L'_2, L_3) \} \quad (62)
\end{aligned}$$

with

$$\begin{aligned}
f_{3a} &= \frac{1}{2M} [(L-M+2)(L-M+1)]^{1/2}, \\
f_{3b} &= \frac{1}{2M} [(L+M+2)(L+M+1)]^{1/2}, \\
f_{3c} &= \frac{1}{2M'} [(L-M'+2)(L-M'+1)]^{1/2}, \\
f_{3d} &= \frac{1}{2M'} [(L+M'+2)(L+M'+1)]^{1/2} \quad (63)
\end{aligned}$$

The first kind of integrals over spherical harmonics are:

$$\int_0^\pi \int_0^{2\pi} Y_{L+1}^{M_1+M_2+M_3}(\theta_1, \phi_1) d\Omega_1 = \delta(L+1, 0) \delta(M_1+M_2+M_3, 0) = 0 \quad (64)$$

These integrals are zero because $L \geq 0$. The following integrals are evaluated integrating over the associate Legendre functions :

$$\begin{aligned} A_{Y1}(L, M+n, -n) &= \int_0^\pi \int_0^{2\pi} Y_L^{M+n}(\theta_1, \phi_1) e^{-ni\phi_1} d\Omega_1 \\ &= \pi^{1/2} (2L+1)^{1/2} \left[\frac{(L-M-n)!}{(L+M+n)!} \right]^{1/2} \int_0^\pi P_L^{M+n}(\cos \theta_1) \sin \theta_1 d\theta_1 \end{aligned} \quad (65)$$

using the algorithm developed by Wong [18], in which the overlap integral over Associate Legendre functions is:

$$\begin{aligned} \int_0^\pi P_{L_1}^{M_1}(\cos \theta) P_{L_2}^{M_2}(\cos \theta) \sin(\theta) d\theta &= \sum_{p_1=0}^{p_1 \max} \sum_{p_2=0}^{p_2 \max} a_{L_1, M_1}^{p_1} a_{L_2, M_2}^{p_2} \\ &\times \frac{\Gamma\left(\frac{1}{2}(L_1+L_2-M_1-M_2-2p_1-2p_2+1)\right) \Gamma\left(\frac{1}{2}(M_1+M_2+2p_1+2p_2+2)\right)}{\Gamma\left(\frac{1}{2}(L_1+L_2+3)\right)}. \end{aligned} \quad (66)$$

Γ are Gamma functions. $p_{\max} = [(l-m)/2]$ the integral part of $(l-m)/2$. This formula is valid for $0 \leq M_1 \leq L_1$ and $0 \leq M_2 \leq L_2$. For $M_1 \leq L_1$ or $M_1 \leq L_1$ the integral is zero, see Ref. [18]. If M is negative the formula is used:

$$P_L^{-M}(\cos \theta_1) = (-1)^M \frac{(L-M)!}{(L+M)!} P_L^M(\cos \theta_1). \quad (67)$$

For even $L_1+L_2-M_1-M_2$ the integral vanish. The coefficients are:

$$a_{L,M}^p = \frac{(-1)^p (L+M)!}{2^{M+2p} (M+p)! p! (L-M-2p)!}. \quad (68)$$

The radial three-electron integral fulfill the symmetry :

$$\begin{aligned} J(N_1-1, N_2+1, N_3; \omega_1, \omega_2, \omega_3; -1, 1; L_2, L_3) &= \\ J(N_1-1, N_3, N_2+1; \omega_1, \omega_3, \omega_2; 1, -1; L_3, L_2) \end{aligned}$$

Finally the programmable expression is:

$$\begin{aligned}
I_{KE,\theta_1}(1) = & (4\pi)^{1/2} \sum_{L_1=|l'_1-l_1|}^{l'_1+l_1} \sum_{L_3=|l'_3-l_3|}^{l'_3+l_3} \left\{ \sum_{L_2=|l'_2-1-l_2|}^{l'_2-1+l_2} \sum_{L=|L_2-L_1|}^{L_1+L_2} \sum_{L_4=|L-L_3|}^{L+L_4} \right. \\
& (-1)^{M_2+M_3} \frac{(2L+1)}{(2L+3)^{1/2}} [(2L_1+1)(2L_3+1)(2L_2+1)(2L_4+1)]^{1/2} \\
& (f_{1a}c_{1a}f_{2a}c_{2a}f_{3b}c_{3L_3}c_{4a}c_{5a}A_{Y1}(L+1, M+1, -2) \\
& - f_{1b}c_{1b}f_{2a}c_{2a}f_{3c}c_{3L_3}c_{4b}c_{5b}A_{Y1}(L+1, M'-1, 2)) \\
& \times J(N_1-1, N_3, N_2+1; \omega_1, \omega_3, \omega_2; 1, -1; L_3, L_2) \\
& + \sum_{L'_2=|l'_2+1-l_2|}^{l'_2+1+l_2} \sum_{L'=|L'_2-L_1|}^{L_1+L_2} \sum_{L'_4=|L'-L_3|}^{L'+L_3} (-1)^{M'_2+M_3} \frac{(2L+1)}{(2L+3)^{1/2}} \\
& [(2L_1+1)(2L_3+1)(2L'_2+1)(2L'_4+1)]^{1/2} \\
& (f_{1a}c_{1a}f_{2b}c_{2b}f_{3b}c_{3L_3}c_{4c}c_{5c}A_{Y1}(L'+1, M+1, -2) \\
& - f_{1b}c_{1b}f_{2b}c_{2b}f_{3c}c_{3L_3}c_{4d}c_{5d}A_{Y1}(L'+1, M'-1, 2)) \\
& \left. \times J(N_1-1, N_3, N_2+1; \omega_1, \omega_3, \omega_2; 1, -1; L_3, L'_2) \right\} \quad (69)
\end{aligned}$$

3.2 Evaluation of I_{KE,θ_2}

For the evaluation of I_{KE,θ_2} , the same steps than for I_{KE,θ_1} Eqs. (31-34) are needed. Afterwards the product of spherical harmonics of electron 2 should be linearized. Then a rotation like in Eq. (A.7) is performed and the complex conjugate of $Y_{L_1}^{M_1-1}(\theta_1, \phi_1)$ used. The new products of $Y_{L_1}^{-M_1+1*}(\theta_1, \phi_1)Y_{L_2}^{M_2}(\theta_1, \phi_1)$ lead to:

$$\begin{aligned}
& \left(Y_{l_3}^{m_3*}(\theta_2, \phi_2) Y_{l'_3}^{m'_3}(\theta_2, \phi_2) \right) \left(Y_{l_2}^{m_2*}(\theta_2, \phi_2) Y_{l'_2}^{m'_2}(\theta_2, \phi_2) \right) \\
& \times \left(Y_{l_1}^{m_1*}(\theta_1, \phi_1) \frac{\partial Y_{l'_1}^{m'_1}(\theta_1, \phi_1)}{\partial \theta_1} \right) = (4\pi)^{1/2} (-1)^{M_2+M_3} \sum_{L_1=|l'_1-l_1|}^{l'_1+l_1} \sum_{L_2=|l'_2-l_2|}^{l'_2+l_2} \sum_{L_3=|l'_3-l_3|}^{l'_3+l_3} \\
& \sum_{L=|L_1-L_2|}^{L_1+L_2} \sum_{L'=|L-L_3|}^{L+L_3} [(2L_1+1)(2L_2+1)(2L_3+1)(2L+1)(2L'+1)]^{1/2} c_{2L_2}c_{3L_3} \\
& \times \left\{ f_{1a}c_{1a}c_{2a}Y_{L'}^{M_1+M_2+M_3+1}(\theta_1, \phi_1)e^{-i\phi_1} \right. \\
& \left. - f_{1b}c_{1b}c_{2b}Y_{L'}^{M_1+M_2+M_3-1}(\theta_1, \phi_1)e^{i\phi_1} \right\} \quad (70)
\end{aligned}$$

where

$$\begin{aligned} c_{2L_2} &= C^{L_2}(l'_2, m'_2; l_2, m_2), & c_{3L_3} &= C^{L_3}(l'_3, m'_3; l_3, m_3) \\ c_{2a} &= C^L(L_1, M_1 + 1; L_2, -M_2), & c_{2b} &= C^L(L_1, M_1 - 1; L_2, -M_2) \end{aligned} \quad (71)$$

$$c_{3a} = C^{L'}(L_1, M_1 + 1; L_3, -M_3), \quad c_{3b} = C^{L'}(L_1, M_1 - 1; L_3, -M_3) \quad (72)$$

Now we apply the recursion relation including the $\cot \theta$ function [?, 5.7.]:

$$\begin{aligned} -\cot \theta_1 Y_{l'_1}^{m'_1}(\theta_1, \phi_1) &= \frac{1}{2m'_1} [(l + m + 1)(l - m)]^{1/2} e^{-i\phi_1} Y_l^{m+1}(\theta_1, \phi_1) \\ &+ \frac{1}{2m'_1} [(l - m + 1)(l + m)]^{1/2} e^{i\phi_1} Y_l^{m-1}(\theta_1, \phi_1) \end{aligned} \quad (73)$$

which leads to:

$$\begin{aligned} I_{KE, \theta_1, 2} &= \sqrt{\pi} (-1)^{M_2 + M_3} \sum_{L_1=|l'_1-l_1|}^{l'_1+l_1} \sum_{L_2=|l'_2-l_2|}^{l'_2+l_2} \sum_{L_3=|l'_3-l_3|}^{l'_3+l_3} \sum_{L=|L_1-L_2|}^{L_1+L_2} \sum_{L'=|L-L_3|}^{L+L_3} \\ &[(2L_1 + 1)(2L_2 + 1)(2L_3 + 1)(2L + 1)(2L' + 1)]^{1/2} c_{2L_2} c_{2L_3} \\ &\times \left\{ f_{1a} c_{1a} f_{2a} c_{2a} c_{3a} \int_0^\pi \int_0^{2\pi} Y_{L'}^{M_1+M_2+M_3+2}(\theta_1, \phi_1) e^{-2i\phi_1} d\Omega_1 \right. \\ &\quad + f_{1a} c_{1a} f_{2b} c_{2a} c_{3a} \int_0^\pi \int_0^{2\pi} Y_{L'}^{M_1+M_2+M_3}(\theta_1, \phi_1) d\Omega_1 \\ &\quad - f_{1b} c_{1b} f_{2c} c_{2b} c_{3b} \int_0^\pi \int_0^{2\pi} Y_{L'}^{M_1+M_2+M_3}(\theta_1, \phi_1) d\Omega_1 \\ &\quad \left. - f_{1b} c_{1b} f_{2d} c_{2b} c_{3b} \int_0^\pi \int_0^{2\pi} Y_{L'}^{M_1+M_2+M_3-2}(\theta_1, \phi_1) e^{2i\phi_1} d\Omega_1 \right\} \\ &\times [J(N_1 - 2, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, 1; L_2, L_3) \\ &\quad - J(N_1, N_2; N_3; \omega_1, \omega_2, \omega_3; -1, 1; L_2, L_3) \\ &\quad - J(N_1 - 2, N_2 + 2, N_3; \omega_1, \omega_2, \omega_3; -1, 1; L_2, L_3)], \end{aligned} \quad (74)$$

with $M = M_1 + M_2 + M_3 + 1$ and $M' = M_1 + M_2 + M_3 - 1$. Integrating:

$$\begin{aligned}
f_{2a} &= \frac{1}{2M}[(L' + M + 1)(L' - M)]^{1/2}, \\
f_{2b} &= \frac{1}{2M}[(L' - M + 1)(L' + M)]^{1/2}, \\
f_{2c} &= \frac{1}{2M'}[(L' + M' + 1)(L' - M')]^{1/2}, \\
f_{2d} &= \frac{1}{2M'}[(L' + M' + 1)(L' + M')]^{1/2} \quad (75)
\end{aligned}$$

Using Eqs.(46-49), and the symmetry property of the radial three-electron integrals, the final programmable expression is:

$$\begin{aligned}
I_{KE,\theta_1,2} &= \sqrt{\pi}(-1)^{M_2+M_3} \sum_{L_1=|l'_1-l_1|}^{l'_1+l_1} \sum_{L_2=|l'_2-l_2|}^{l'_2+l_2} \sum_{L_3=|l'_3-l_3|}^{l'_3+l_3} \sum_{L=|L_1-L_2|}^{L_1+L_2} \sum_{L'=|L-L_3|}^{L+L_3} \\
&\quad [(2L_1 + 1)(2L_2 + 1)(2L_3 + 1)(2L + 1)(2L' + 1)]^{1/2} c_{2L_2} c_{2L_3} \\
&\quad \times \{ f_{1a} c_{1a} f_{2a} c_{2a} c_{3a} A_{Y1}(L', M + 1, -2) \\
&\quad + \delta_{(L',0)} \delta_{(M_1+M_2+M_3,0)} (f_{1a} c_{1a} f_{2b} c_{2a} c_{3a} - f_{1b} c_{1b} f_{2c} c_{2b} c_{3b}) \\
&\quad - f_{1b} c_{1b} f_{2d} c_{2b} c_{3b} A_{Y1}(L', M - 1, 2) \} \\
&\quad \times [J(N_1 - 2, N_2, N_3; \omega_1, \omega_2, \omega_3; 1, 1; L_2, L_3) \\
&\quad - J(N_1, N_2; N_3; \omega_1, \omega_2, \omega_3; -1, 1; L_2, L_3) \\
&\quad - J(N_1 - 2, N_2 + 2, N_3; \omega_1, \omega_2, \omega_3; -1, 1; L_2, L_3)], \quad (76)
\end{aligned}$$

3.3 Evaluation of $I_{KE,\phi 3}$

The derivative of the spherical harmonic with $m'_1 = 0$ with respect to ϕ_1 vanishes:

$$I_{KE,\phi_1,3} = 0. \quad (77)$$

In case of $m_1 \neq 0$:

$$\frac{\partial Y_l^m(\theta, \phi)}{\partial \phi} = im Y_l^m(\theta, \phi). \quad (78)$$

In this section we evaluate Eq. (30). The function $\sin(\phi_1 - \phi_2)$ can be written in exponential form:

$$\sin(\phi_1 - \phi_2) = \frac{1}{2i} (e^{i\phi_1} e^{-i\phi_2} - e^{-i\phi_1} e^{i\phi_2}), \quad (79)$$

and the following functions can be written as spherical harmonics:

$$\sin \theta_2 e^{-i\phi_2} = \sqrt{\frac{8\pi}{3}} Y_1^{-1}(\theta_2, \phi_2), \quad \sin \theta_2 e^{i\phi_2} = -\sqrt{\frac{8\pi}{3}} Y_1^1(\theta_2, \phi_2). \quad (80)$$

The products of spherical harmonics can be linearized:

$$\begin{aligned} \sqrt{\frac{8\pi}{3}} Y_{l_2}^{m_{2*}}(\theta_2, \phi_2) Y_1^{-1}(\theta_2, \phi_2) &= \sqrt{\frac{2}{3}} \sum_{L_2=|l_2-1|}^{l_2+1} (2L_2+1)^{1/2} c_{2a} Y_{L_2}^{-1-m_2}(\theta_2, \phi_2) \\ \sqrt{\frac{8\pi}{3}} Y_{l_2}^{m_{2*}}(\theta_2, \phi_2) Y_1^1(\theta_2, \phi_2) &= \sqrt{\frac{2}{3}} \sum_{L_2=|l_2-1|}^{l_2+1} (2L_2+1)^{1/2} c_{2b} Y_{L_2}^{1-m_2}(\theta_2, \phi_2) \end{aligned} \quad (81)$$

with

$$c_{2a} = C^{L_2}(1, -1; l_2, m_2), \quad c_{2b} = C^{L_2}(1, 1; l_2, m_2). \quad (82)$$

Using the above derived expression, the product of angular functions is:

$$\begin{aligned} &\left(-Y_{l_1}^{m_{1*}}(\theta_1, \phi_1) Y_{l_2}^{m_2}(\theta_2, \phi_2) \frac{\sin \theta_2}{\sin \theta_1} \sin(\phi_1 - \phi_2) \frac{\partial Y_{l'_1}^{m'_1}(\theta_1, \phi_1)}{\partial \phi_1} Y_{l'_2}^{m'_2}(\theta_2, \phi_2) \right) \\ &\quad \times (Y_{l_3}^{m_{3*}}(\theta_3, \phi_3) Y_{l_3}^{m_3}(\theta_3, \phi_3)) = \\ &\quad \frac{1}{(4\pi)^{1/2}} \frac{m_1}{2} \sqrt{\frac{2}{3}} \sum_{L_3=|l'_3-l_3|}^{l'_3+l_3} \sum_{L_2=|l_2-1|}^{l_2+1} [(2L_2+1)(2L_3+1)]^{1/2} c_{3L_3} Y_{L_3}^{M_3}(\theta_3, \phi_3) \\ &\quad \times \left\{ c_{2a} Y_{L_2}^{-1-m_2}(\theta_1, \phi_1) Y_{l'_1}^{m_1}(\theta_1, \phi_1) \frac{e^{i\phi_1}}{\sin \theta_1} Y_{l'_1}^{m'_1}(\theta_1, \phi_1) Y_{l'_2}^{m'_2}(\theta_2, \phi_2) \right. \\ &\quad \left. + c_{2b} Y_{L_2}^{1-m_2}(\theta_1, \phi_1) Y_{l'_1}^{m_1}(\theta_1, \phi_1) \frac{e^{-i\phi_1}}{\sin \theta_1} Y_{l'_1}^{m'_1}(\theta_1, \phi_1) Y_{l'_2}^{m'_2}(\theta_2, \phi_2) \right\}, \quad (83) \end{aligned}$$

with $c_{3L_3} = C^{L_3}(l'_3, m'_3; l_3, m_3)$. Using the recursion relation containing the sinus function Eq. (42) over $Y_{l'_1}^{m'_1}(\theta_1, \phi_1)$ (this relation can be always used directly over $Y_{l'_1}^{m'_1}(\theta_1, \phi_1)$ because by definition $m'_1 \neq 0$, for $m'_1 = 0$, the derivative of a spherical harmonic is zero, see Eq. (xx)) and the factors defined as:

$$f_{1a} = [(l'_1 - m'_1 + 2)(l'_1 - m'_1 + 1)]^{1/2}, \quad f_{1b} = [(l'_1 + m'_1 + 2)(l'_1 + m'_1 + 1)]^{1/2} \quad (84)$$

Eq. (63) can be written:

$$\begin{aligned} & (-1)^{m'_2} \frac{1}{(4\pi)^{1/2}} \frac{1}{4} \sqrt{\frac{2}{3}} \left[\frac{2l'_1 + 1}{2l'_1 + 3} \right]^{1/2} \sum_{L_3=|l'_3-l_3|}^{l'_3+l_3} \sum_{L_2=|l_2-1|}^{l_2+1} [(2L_2 + 1)(2L_3 + 1)]^{1/2} \\ & \times c_{3L_3} Y_{L_3}^{M_3}(\theta_3, \phi_3) \left\{ c_{2a} Y_{l'_2}^{m'_2}(\theta_2, \phi_2) Y_{L_2}^{-1-m_2}(\theta_2, \phi_2) \right. \\ & \times \left(f_{1a} Y_{l'_1}^{m_1}(\theta_1, \phi_1) e^{2\phi_1} Y_{l'_1+1}^{m'_1-1}(\theta_1, \phi_1) + f_{1b} Y_{l'_1}^{m_1}(\theta_1, \phi_1) Y_{l'_1+1}^{m'_1+1}(\theta_1, \phi_1) \right) \\ & \left. + c_{2b} Y_{l'_2}^{m'_2}(\theta_2, \phi_2) Y_{L_2}^{1-m_2}(\theta_2, \phi_2) \right. \\ & \times \left(f_{1a} Y_{l'_1}^{m_1}(\theta_1, \phi_1) Y_{l'_1+1}^{m'_1-1}(\theta_1, \phi_1) + f_{1b} Y_{l'_1}^{m_1}(\theta_1, \phi_1) e^{-2\phi_1} Y_{l'_1+1}^{m'_1+1}(\theta_1, \phi_1) \right) \left. \right\} \quad (85) \end{aligned}$$

Combining $Y_{l'_2}^{m'_2}(\theta_2, \phi_2) Y_{L_2}^{-1-m_2}(\theta_2, \phi_2)$:

$$\begin{aligned} Y_{l'_2}^{m'_2}(\theta_2, \phi_2) Y_{L_2}^{-1-m_2}(\theta_2, \phi_2) &= (-1)^{m'_2} \sum_{L'_2=|L_2-l'_2|}^{L_2+l'_2} \frac{(2L'_2 + 1)^{1/2}}{(4\pi)^{1/2}} c_{2L'a} Y_{L'_2}^{M_2-1}(\theta_2, \phi_2) \\ Y_{l'_2}^{m'_2}(\theta_2, \phi_2) Y_{L_2}^{1-m_2}(\theta_2, \phi_2) &= (-1)^{m'_2} \sum_{L'_2=|L_2-l'_2|}^{L_2+l'_2} \frac{(2L'_2 + 1)^{1/2}}{(4\pi)^{1/2}} c_{2L'b} Y_{L'_2}^{M_2+1}(\theta_2, \phi_2) \quad (86) \end{aligned}$$

with

$$c_{2L'a} = C^{L'_2}(L_2, -1 - m_2; l'_2, -m'_2), \quad c_{2L'b} = C^{L'_2}(L_2, 1 - m_2; l'_2, -m'_2) \quad (87)$$

Eq. (65) can be rewritten as:

$$\begin{aligned} & (-1)^{m'_2} \frac{1}{4\pi} \frac{1}{4} \sqrt{\frac{2}{3}} \left[\frac{2l'_1 + 1}{2l'_1 + 3} \right]^{1/2} \sum_{L_3=|l'_3-l_3|}^{l'_3+l_3} \sum_{L_2=|l_2-1|}^{l_2+1} \sum_{L'_2=|L_2-l'_2|}^{L_2+l'_2} \sum_{L_1=|l'_1+1-l_1|}^{l'_1+1+l_1} \\ & \times [(2L_1 + 1)(2L_2 + 1)(2L_3 + 1)(2L'_2 + 1)]^{1/2} \\ & \times \left\{ c_{2a} c_{2L'a} c_{3L_3} Y_{L_3}^{M_3}(\theta_3, \phi_3) Y_{L'_2}^{M_2-1}(\theta_2, \phi_2) \right. \\ & \times \left(f_{1a} c_{1a} Y_{L_1}^{M_1-1}(\theta_1, \phi_1) e^{2\phi_1} + f_{1b} c_{1b} Y_{L_1}^{M_1+1}(\theta_1, \phi_1) \right) \\ & \left. + c_{2b} c_{2L'b} c_{3L_3} Y_{L_3}^{M_3}(\theta_3, \phi_3) Y_{L'_2}^{M_2+1}(\theta_2, \phi_2) \right. \\ & \left. \left(f_{1a} c_{1a} Y_{L_1}^{M_1-1}(\theta_1, \phi_1) + f_{1b} c_{1b} Y_{L_1}^{M_1+1}(\theta_1, \phi_1) e^{-2\phi_1} \right) \right\}, \quad (88) \end{aligned}$$

with

$$c_{1a} = C^{L_1}(l'_1 + 1, m'_1 - 1; l_1, m_1), \quad c_{1b} = C^{L_1}(l'_1 + 1, m'_1 + 1; l_1, m_1). \quad (89)$$

After a rotation of the spherical harmonics of electron 2, see Eq. (A.7):

$$\begin{aligned} I_{KE, \phi_1, 3} = & (-1)^{m'_2} \frac{1}{4\pi} \frac{1}{4} \sqrt{\frac{2}{3}} \left[\frac{2l'_1 + 1}{2l'_1 + 3} \right]^{1/2} \sum_{L_3=|l'_3-l_3|}^{l'_3+l_3} \sum_{L_2=|l_2-1|}^{l_2+1} \sum_{L'_2=|L_2-l'_2|}^{L_2+l'_2} \sum_{L_1=|l'_1+1-l_1|}^{l'_1+1+l_1} \\ & \times [(2L_1 + 1)(2L_2 + 1)(2L_3 + 1)(2L'_2 + 1)]^{1/2} c_{3L_3} Y_{L_3}^{M_3}(\theta_3, \phi_3) \{ c_{2a} c_{2L'a} \\ & \times \left(f_{1a} c_{1a} \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1-1}(\theta_1, \phi_1) Y_{L'_2}^{M_2-1}(\theta_1, \phi_1) e^{2\phi_1} d\Omega_1 \right. \\ & \left. + f_{1b} c_{1b} \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1+1}(\theta_1, \phi_1) Y_{L'_2}^{M_2-1}(\theta_1, \phi_1) d\Omega_1 \right) \\ & + c_{2b} c_{2L'b} \left(f_{1a} c_{1a} \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1-1}(\theta_1, \phi_1) Y_{L'_2}^{M_2+1}(\theta_1, \phi_1) d\Omega_1 \right. \\ & \left. + f_{1b} c_{1b} \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1+1}(\theta_1, \phi_1) Y_{L'_2}^{M_2+1}(\theta_1, \phi_1) e^{-2\phi_1} d\Omega_1 \right) \} \quad (90) \end{aligned}$$

rotating $Y_{L_3}^{M_3}(\theta_3, \phi_3)$ we obtain $4\pi Y_{L_3}^{M_3}(\theta_1, \phi_1)$:

$$\begin{aligned} I_{KE, \phi_1, 3} = & (-1)^{m'_2} \frac{1}{4} \sqrt{\frac{2}{3}} \left[\frac{2l'_1 + 1}{2l'_1 + 3} \right]^{1/2} \sum_{L_3=|l'_3-l_3|}^{l'_3+l_3} \sum_{L_2=|l_2-1|}^{l_2+1} \sum_{L'_2=|L_2-l'_2|}^{L_2+l'_2} \sum_{L_1=|l'_1+1-l_1|}^{l'_1+1+l_1} \\ & \times [(2L_1 + 1)(2L_2 + 1)(2L_3 + 1)(2L'_2 + 1)]^{1/2} \{ c_{2a} c_{2L'a} c_{3L_3} \\ & \times \left(f_{1a} c_{1a} \int_0^\pi \int_0^{2\pi} Y_{L_3}^{M_3}(\theta_1, \phi_1) Y_{L_1}^{M_1-1}(\theta_1, \phi_1) Y_{L'_2}^{M_2-1}(\theta_1, \phi_1) e^{2\phi_1} d\Omega_1 \right. \\ & \left. + f_{1b} c_{1b} \int_0^\pi \int_0^{2\pi} Y_{L_3}^{M_3}(\theta_1, \phi_1) Y_{L_1}^{M_1+1}(\theta_1, \phi_1) Y_{L'_2}^{M_2-1}(\theta_1, \phi_1) d\Omega_1 \right) \\ & + c_{2b} c_{2L'b} c_{3L_3} \left(f_{1a} c_{1a} \int_0^\pi \int_0^{2\pi} Y_{L_3}^{M_3}(\theta_1, \phi_1) Y_{L_1}^{M_1-1}(\theta_1, \phi_1) Y_{L'_2}^{M_2+1}(\theta_1, \phi_1) d\Omega_1 \right. \\ & \left. + f_{1b} c_{1b} \int_0^\pi \int_0^{2\pi} Y_{L_3}^{M_3}(\theta_1, \phi_1) Y_{L_1}^{M_1+1}(\theta_1, \phi_1) Y_{L'_2}^{M_2+1}(\theta_1, \phi_1) e^{-2\phi_1} d\Omega_1 \right) \} \quad (91) \end{aligned}$$

taking the complex conjugate and using the product theorem:

$$\begin{aligned}
I_{KE,\phi_1,3} = & (-1)^{m'_2+M_3} \frac{1}{8} \sqrt{\frac{2}{3\pi}} \left[\frac{2l'_1+1}{2l'_1+3} \right]^{1/2} \sum_{L_3=|l'_3-l_3|}^{l'_3+l_3} \sum_{L_2=|l_2-1|}^{l_2+1} \sum_{L'_2=|L_2-l'_2|}^{L_2+l'_2} \sum_{L_1=|l'_1+1-l_1|}^{l'_1+1+l_1} \\
& \sum_{L'_3=|L_3-L'_2|}^{L_3+L'_2} [(2L_1+1)(2L_2+1)(2L_3+1)(2L'_2+1)(2L'_3+1)]^{1/2} \{ c_{2a} c_{2L'a} c_{3L_3} \\
& \times \left(f_{1a} c_{1a} c_{3a} \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1-1}(\theta_1, \phi_1) Y_{L'_3}^{M_2+M_3-1}(\theta_1, \phi_1) e^{2\phi_1} d\Omega_1 \right. \\
& \quad \left. + f_{1b} c_{1b} c_{3b} \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1+1}(\theta_1, \phi_1) Y_{L'_3}^{M_2+M_3-1}(\theta_1, \phi_1) d\Omega_1 \right) \\
& + c_{2b} c_{2L'b} c_{3L_3} \left(f_{1a} c_{1a} c_{3a} \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1-1}(\theta_1, \phi_1) Y_{L'_3}^{M_2+M_3+1}(\theta_1, \phi_1) d\Omega_1 \right. \\
& \quad \left. + f_{1b} c_{1b} c_{3b} \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1+1}(\theta_1, \phi_1) Y_{L'_3}^{M_2+M_3+1}(\theta_1, \phi_1) e^{-2\phi_1} d\Omega_1 \right) \} \quad (92)
\end{aligned}$$

with

$$c_{3a} = C^{L'_3}(L'_2, M_2 + 1; L_3, -M_3), \quad c_{3b} = C^{L'_3}(L'_2, M_2 - 1; L_3, -M_3). \quad (93)$$

And defining the new auxiliary angular integral:

$$\begin{aligned}
A_{Y2}(L_1, M_1 + n, L_2, M_2 + n, -2n) &= \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1+n}(\theta, \phi) Y_{L_2}^{M_2+n}(\theta, \phi) e^{-2ni\phi} d\Omega \\
&= \frac{1}{2} [(2L_1+1)(2L_2+1)]^{1/2} \left[\frac{(L_1 - M_1 - n)!}{(L_1 + M_1 + n)!} \right] \\
&\quad \times \int_0^\pi P_{L_1}^{M_1+n}(\cos \theta) P_{L_2}^{M_2+n}(\cos \theta) \sin \theta d\theta \quad (94)
\end{aligned}$$

This integral of the product of Legendre polynomials is solved according the Eq. (47) from Wong, finally the integral is:

$$\begin{aligned}
I_{KE,\phi_1,3} = & (-1)^{m'_2+M_3} \frac{1}{8} \sqrt{\frac{2}{3\pi}} \left[\frac{2l'_1+1}{2l'_1+3} \right]^{1/2} \sum_{L_3=|l'_3-l_3|}^{l'_3+l_3} \sum_{L_2=|l_2-1|}^{l_2+1} \sum_{L'_2=|L_2-l'_2|}^{L_2+l'_2} \sum_{L_1=|l'_1+1-l_1|}^{l'_1+1+l_1} \\
& \sum_{L'_3=|L_3-L'_2|}^{L_3+L'_2} [(2L_1+1)(2L_2+1)(2L_3+1)(2L'_2+1)(2L'_3+1)]^{1/2} \{ c_{2a} c_{2L'a} c_{3L_3} \\
& \times (f_{1a} c_{1a} c_{3a} A_{Y2}(L_1, M_1-1, L'_3, M_2+M_3-1, 2) \\
& + f_{1b} c_{1b} c_{3b} (-1)^{M_1+1} \delta(L_1, L'_3) \delta(M_1+1, M_2+M_3-1)) \\
& + c_{2b} c_{2L'b} c_{3L_3} (f_{1a} c_{1a} c_{3a} (-1)^{M_1-1} \delta(L_1, L'_3) \delta(M_1-1, M_2+M_3+1) \\
& + f_{1b} c_{1b} c_{3b} A_{Y2}(L_1, M_1+1, L'_2, M_2+1, -2)) \} \quad (95)
\end{aligned}$$

We have developed a computer code and computed the radial integral equations Eq. (24-26) and angular integral contributions to the kinetic energy Eqs. (27,50,56,72). The computer code has quadruple precision. In Table 1 we show some selected values of two-electron kinetic energy integrals calculated with high precision. The integrals of Table 1 have been checked with the ones calculated using the Kolos and Roothaan transformation, agreeing to more than 30 decimal digits. Finally, in Table 2 several kinetic energy integrals have been decomposed in all their components.

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Appendix A: connexion to KR method. Why the KR method cannot be extended to three-electron integrals

The derivative of r_{12}^ν is:

$$\nabla_1 r_{12}^\nu = -\nabla_2 r_{12}^\nu = \nabla_{12} r_{12}^\nu = \nu r_{12}^{\nu-1} \frac{\vec{r}_{12}}{r_{12}} \quad (\text{A.1})$$

Short proof:

$$\nabla_1 \equiv \vec{\nabla}_1 = \frac{\partial}{\partial x_1} \vec{i} + \frac{\partial}{\partial y_1} \vec{j} + \frac{\partial}{\partial z_1} \vec{k} \quad (\text{A.2})$$

the interelectronic distance in Cartessian coordinates:

$$r_{12} = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2} \quad (\text{A.3})$$

$$\begin{aligned} \left(\frac{\partial}{\partial x_1} \vec{i} + \frac{\partial}{\partial x_1} \vec{j} + \frac{\partial}{\partial x_1} \vec{k} \right) r_{12} = \\ \frac{1}{r_{12}} \left[(x_1 - x_2) \vec{i} + (y_1 - y_2) \vec{j} + (z_1 - z_2) \vec{k} \right] = \frac{\vec{r}_1 - \vec{r}_2}{r_{12}} = \frac{\vec{r}_{12}}{r_{12}} \end{aligned} \quad (\text{A.4})$$

The scalar product of a vector with itself:

$$\frac{\vec{r}_{12}}{r_{12}} \cdot \frac{\vec{r}_{12}}{r_{12}} = \frac{|\vec{r}_{12}|^2}{r_{12}^2} = \frac{r_{12}^2}{r_{12}^2} = 1 \quad (\text{A.5})$$

In the case of the two-electron kinetic energy integrals we can make use of the property Eq. (10) and to obtain the expressions in terms of radial coordinates r_{12} :

$$\begin{aligned} \int [\phi_1^*(\mathbf{r}_1) r_{12}^\nu \nabla_1^*] [\nabla_1 r_{12}^{\nu'} \phi_1'(\mathbf{r}_1)] d\tau_1 = \\ = \nu \nu' \int \phi_1^*(\mathbf{r}_1) \phi_1'(\mathbf{r}_1) r_{12}^{\nu+\nu'-2} \frac{\vec{r}_{12}}{r_{12}} \frac{\vec{r}_{12}}{r_{12}} d\tau_1 \\ + \int r_{12}^{\nu+\nu'} [\nabla_1 \phi_1^*(\mathbf{r}_1)] [\nabla_1 \phi_1'(\mathbf{r}_1)] r_{12}^{\nu+\nu'} d\tau_1 \\ + \nu \int [\phi_1^*(\mathbf{r}_1) \nabla_1 \phi_1'(\mathbf{r}_1)] r_{12}^{\nu+\nu'-1} \frac{\vec{r}_{12}}{r_{12}} d\tau_1 \\ + \nu' \int [\phi_1'(\mathbf{r}_1) \nabla_1 \phi_1^*(\mathbf{r}_1)] r_{12}^{\nu+\nu'-1} \frac{\vec{r}_{12}}{r_{12}} d\tau_1 \end{aligned} \quad (\text{A.6})$$

The three-electron kinetic energy integral:

$$- \langle \phi_1(\mathbf{r}_1) \phi_2(\mathbf{r}_2) \phi_3(\mathbf{r}_3) r_{12} | \nabla_1^2 | \phi_1'(\mathbf{r}_1) \phi_2'(\mathbf{r}_2) \phi_3'(\mathbf{r}_3) r_{13} \rangle = \\ \int \phi_2^*(\mathbf{r}_2) \phi_2'(\mathbf{r}_2) d\tau_2 \int \phi_3^*(\mathbf{r}_3) \phi_3'(\mathbf{r}_3) d\tau_3 \int [\phi_1^*(\mathbf{r}_1) r_{12} \nabla_1^*] [\nabla_1 r_{13} \phi_1'(\mathbf{r}_1)] d\tau_1 \quad (\text{A.7})$$

using the turn over rule of the antihermitian operator nabla:

$$\nabla^* = -\nabla \quad (\text{A.8})$$

$$I = \int [\phi_1^*(\mathbf{r}_1) r_{12} \nabla_1^*] [\nabla_1 r_{13} \phi_1'(\mathbf{r}_1)] d\tau_1 \quad (\text{A.9})$$

the derivative of a product:

$$\begin{aligned} \nabla_1^* \phi_1^*(\mathbf{r}_1) r_{12} &= r_{12} \nabla_1^* \phi_1^*(\mathbf{r}_1) + \phi_1^*(\mathbf{r}_1) \nabla_1^* r_{12} \\ \nabla_1 r_{13} \phi_1'(\mathbf{r}_1) &= r_{13} \nabla_1 \phi_1'(\mathbf{r}_1) + \phi_1'(\mathbf{r}_1) \nabla_1 r_{13} \end{aligned} \quad (\text{A.10})$$

$$\begin{aligned} - \int [\phi_1^*(\mathbf{r}_1) r_{12} \nabla_1^*] [\nabla_1 r_{13} \phi_1'(\mathbf{r}_1)] d\tau_1 &= \\ \int r_{12} r_{13} [\nabla_1^* \phi_1^*(\mathbf{r}_1)] [\nabla_1 \phi_1'(\mathbf{r}_1)] d\tau_1 &+ \int \phi_1^*(\mathbf{r}_1) \phi_1'(\mathbf{r}_1) [\nabla_1^* r_{12}] [\nabla_1 r_{13}] d\tau_1 \\ + \int [\phi_1^*(\mathbf{r}_1) \nabla_1 \phi_1'(\mathbf{r}_1)] [r_{13} \nabla_1 r_{12}] d\tau_1 &+ \int [\phi_1'(\mathbf{r}_1) \nabla_1^* \phi_1^*(\mathbf{r}_1)] [r_{12} \nabla_1 r_{13}] d\tau_1 \end{aligned} \quad (\text{A.11})$$

Let us evaluate first the integral $\int \phi_1^*(\mathbf{r}_1) \phi_1'(\mathbf{r}_1) [\nabla_1^* r_{12}] [\nabla_1 r_{13}] d\tau_1$:

$$\int \phi_1^*(\mathbf{r}_1) \phi_1'(\mathbf{r}_1) [\nabla_1^* r_{12}] [\nabla_1 r_{13}] d\tau_1 = \int \phi_1^*(\mathbf{r}_1) \phi_1'(\mathbf{r}_1) \frac{\vec{r}_{12}}{r_{12}} \cdot \frac{\vec{r}_{13}}{r_{13}} d\tau_1 \quad (\text{A.12})$$

the scalar product of the two vectors \vec{r}_{12} and \vec{r}_{13} leads to:

$$\begin{aligned} \vec{r}_{12} \cdot \vec{r}_{13} &= \left[(x_1 - x_2) \vec{i} + (y_1 - y_2) \vec{j} + (z_1 - z_2) \vec{k} \right] \\ &\quad \times \left[(x_1 - x_3) \vec{i} + (y_1 - y_3) \vec{j} + (z_1 - z_3) \vec{k} \right] \\ &= (x_1 - x_2)(x_1 - x_3) + (y_1 - y_2)(y_1 - y_3) + (z_1 - z_2)(z_1 - z_3) \end{aligned} \quad (\text{A.13})$$

For simplicity, let us consider only the coordinates x :

$$(x_1 - x_2)(x_1 - x_3) = x_1^2 - x_1x_2 - x_1x_3 + x_2x_3 \quad (\text{A.14})$$

together with the coordinates y and z , it can be transformed to:

$$\vec{r}_{12} \cdot \vec{r}_{13} = \frac{1}{2} (r_{12}^2 + r_{13}^2 - r_{23}^2) \quad (\text{A.15})$$

so the integral is transformed to:

$$\begin{aligned} \int \phi_1^*(\mathbf{r}_1) \phi_1'(\mathbf{r}_1) [\nabla_1^* r_{12}] [\nabla_1 r_{13}] d\tau_1 &= \int \phi_1^*(\mathbf{r}_1) \phi_1'(\mathbf{r}_1) \frac{\vec{r}_{12}}{r_{12}} \cdot \frac{\vec{r}_{13}}{r_{13}} d\tau_1 = \\ &= \frac{1}{2} \int \phi_1^*(\mathbf{r}_1) \phi_1'(\mathbf{r}_1) \frac{r_{12}}{r_{13}} d\tau_1 \\ &+ \frac{1}{2} \int \phi_1^*(\mathbf{r}_1) \phi_1'(\mathbf{r}_1) \frac{r_{13}}{r_{12}} d\tau_1 - \frac{1}{2} \int \phi_1^*(\mathbf{r}_1) \phi_1'(\mathbf{r}_1) \frac{r_{23}^2}{r_{12}r_{13}} d\tau_1 \end{aligned} \quad (\text{A.16})$$

Note that a new integral type has appeared, namely:

$$\left\langle \frac{r_{23}^2}{r_{12}r_{13}} \right\rangle \quad (\text{A.17})$$

Comparing with the case of the two-electron kinetic energy integrals, where a simple overlap integral was obtained, in the case of the three-electron integrals, the derivatives of the interelectronic coordinates produce an scalar product of two vectors, which is transformed in a more complex relation including interelectronic distances. Problem is the new integral.

Now we study the next integrals:

$$\int [\phi_1^*(\mathbf{r}_1) \nabla_1 \phi_1'(\mathbf{r}_1)] [r_{13} \nabla_1 r_{12}] , \quad \int [\phi_1'(\mathbf{r}_1) \nabla_1^* \phi_1^*(\mathbf{r}_1)] [r_{12} \nabla_1 r_{13}] d\tau_1 \quad (\text{A.18})$$

making use of the rule of a product:

$$\nabla_1 [r_{12}r_{13}] = r_{12} \nabla_1 r_{13} + r_{13} \nabla_1 r_{12} \quad (\text{A.19})$$

we add and substract, for instance, the integral:

$$\int [\phi_1^*(\mathbf{r}_1) \nabla_1 \phi_1'(\mathbf{r}_1)] [r_{12} \nabla_1 r_{13}] d\tau_1 \quad (\text{A.20})$$

combining

$$\begin{aligned} \int [\phi_1^*(\mathbf{r}_1) \nabla_1 \phi_1'(\mathbf{r}_1)] \nabla_1 [r_{13} r_{12}] d\tau_1 &= \int [\phi_1^*(\mathbf{r}_1) \nabla_1 \phi_1'(\mathbf{r}_1)] [r_{13} \nabla_1 r_{12}] d\tau_1 \\ &+ \int [\phi_1^*(\mathbf{r}_1) \nabla_1 \phi_1'(\mathbf{r}_1)] [r_{12} \nabla_1 r_{13}] d\tau_1 \end{aligned} \quad (\text{A.21})$$

considering

$$\int [\phi_1^*(\mathbf{r}_1) \nabla_1 \phi_1'(\mathbf{r}_1)] \nabla_1 [r_{13} r_{12}] d\tau_1 = - \int r_{13} r_{12} \nabla_1 (\phi_1^*(\mathbf{r}_1) \nabla_1 \phi_1'(\mathbf{r}_1)) d\tau_1 \quad (\text{A.22})$$

according to the Green's identity:

$$- \nabla (\psi \nabla \phi) = -\psi \nabla^2 \phi - (\nabla \psi) (\nabla \phi) \quad (\text{A.23})$$

combining:

$$\begin{aligned} \int r_{12} r_{13} [\nabla_1^* \phi_1^*(\mathbf{r}_1)] [\nabla_1 \phi_1'(\mathbf{r}_1)] d\tau_1 - \int r_{13} r_{12} \nabla_1 (\phi_1^*(\mathbf{r}_1) \nabla_1 \phi_1'(\mathbf{r}_1)) d\tau_1 = \\ - \int r_{13} r_{12} \phi_1^*(\mathbf{r}_1) \nabla_1^2 \phi_1'(\mathbf{r}_1) d\tau_1 \end{aligned} \quad (\text{A.24})$$

Alltogether we have:

$$\begin{aligned} - \int [\phi_1^*(\mathbf{r}_1) r_{12} \nabla_1^*] [\nabla_1 r_{13} \phi_1'(\mathbf{r}_1)] d\tau_1 &= - \int r_{13} r_{12} \phi_1^*(\mathbf{r}_1) \nabla_1^2 \phi_1'(\mathbf{r}_1) d\tau_1 \\ &+ \frac{1}{2} \int \phi_1^*(\mathbf{r}_1) \phi_1'(\mathbf{r}_1) \frac{r_{12}}{r_{13}} d\tau_1 + \frac{1}{2} \int \phi_1^*(\mathbf{r}_1) \phi_1'(\mathbf{r}_1) \frac{r_{13}}{r_{12}} d\tau_1 \\ &- \frac{1}{2} \int \phi_1^*(\mathbf{r}_1) \phi_1'(\mathbf{r}_1) \frac{r_{23}^2}{r_{12} r_{13}} d\tau_1 \\ &+ \int [\phi_1'(\mathbf{r}_1) \nabla_1^* \phi_1^*(\mathbf{r}_1)] [r_{12} \nabla_1 r_{13}] d\tau_1 \\ &- \int [\phi_1^*(\mathbf{r}_1) \nabla_1 \phi_1'(\mathbf{r}_1)] [r_{12} \nabla_1 r_{13}] d\tau_1 \end{aligned} \quad (\text{A.25})$$

From this point we cannot proceed as in the two-electron Kolos and Roothaan transformation, because it is not possible to put together the interelectronic distances into a common derivative, with the exception of the steps done already Eqs. (34-39).

Other way to solve the last two integrals is to evaluate them individually. For instance, let's take:

$$\int [\phi'_1(\mathbf{r}_1) \nabla_1^* \phi_1^*(\mathbf{r}_1)] [r_{13} \nabla_1 r_{12}] d\tau_1 = \int r_{13} \phi'_1(\mathbf{r}_1) (\nabla_1^* \phi_1^*(\mathbf{r}_1)) (\nabla_1 r_{12}) d\tau_1 \quad (\text{A.26})$$

The derivative of an orbital, see Ref. [26], Appendix D:

$$\phi_1(\mathbf{r}_1) = r_1^{n_1-1} e^{-\alpha_1 r_1} Y_{l_1}^{m_1}(\theta_1, \phi_1) \quad (\text{A.27})$$

$$\nabla_1 \phi_1(\mathbf{r}_1) = \left(\frac{\partial}{\partial x_1} \vec{i} + \frac{\partial}{\partial y_1} \vec{j} + \frac{\partial}{\partial z_1} \vec{k} \right) \phi_1(\mathbf{r}_1) \quad (\text{A.28})$$

Let's consider the derivative with respect the coordinate x and use the chain rule of differentiation:

$$\frac{\partial \phi_1(\mathbf{r}_1)}{\partial x_1} = \frac{\partial r_1}{\partial x_1} \frac{\partial \phi_1(\mathbf{r}_1)}{\partial r_1} + \frac{\partial \theta_1}{\partial x_1} \frac{\partial \phi_1(\mathbf{r}_1)}{\partial \theta_1} + \frac{\partial \phi_1}{\partial x_1} \frac{\partial \phi_1(\mathbf{r}_1)}{\partial \phi_1} \quad (\text{A.29})$$

The terms with coordinate r_1 :

$$\begin{aligned} (\nabla_1^* \phi_1^*(\mathbf{r}_1)) (\nabla_1 r_{12}) &= \\ \left(\frac{\partial r_1}{\partial x_1} \vec{i} + \frac{\partial r_1}{\partial y_1} \vec{j} + \frac{\partial r_1}{\partial z_1} \vec{k} \right) \left(\frac{\partial r_{12}}{\partial x_1} \vec{i} + \frac{\partial r_{12}}{\partial y_1} \vec{j} + \frac{\partial r_{12}}{\partial z_1} \vec{k} \right) \frac{\partial \phi_1(\mathbf{r}_1)}{\partial r_1} &= \\ \left(\frac{\partial r_1}{\partial x_1} \frac{\partial r_{12}}{\partial x_1} + \frac{\partial r_1}{\partial x_1} \frac{\partial r_{12}}{\partial x_1} + \frac{\partial r_1}{\partial x_1} \frac{\partial r_{12}}{\partial x_1} \right) \frac{\partial \phi_1(\mathbf{r}_1)}{\partial r_1} &= \\ \left(\frac{x_1}{r_1} \frac{(x_1 - x_2)}{r_{12}} + \frac{y_1}{r_1} \frac{(y_1 - y_2)}{r_{12}} + \frac{z_1}{r_1} \frac{(z_1 - z_2)}{r_{12}} \right) \frac{\partial \phi_1(\mathbf{r}_1)}{\partial r_1} &= \\ \frac{r_{12}^2 + r_1^2 - r_2^2}{2r_1 r_2} \frac{\partial \phi_1(\mathbf{r}_1)}{\partial r_1} & \quad (\text{A.30}) \end{aligned}$$

The factor:

$$\frac{r_{12}^2 + r_1^2 - r_2^2}{2r_1 r_2} \quad (\text{A.31})$$

appears in Ref. [26] Appendix C and Ref. [14] Eq. (55).

$$\begin{aligned} \int r_{12} \phi'_1(\mathbf{r}_1) (\nabla_1^* \phi_1^*(\mathbf{r}_1)) \nabla_1 r_{13} d\tau_1 &= \int r_{12} \phi'_1(\mathbf{r}_1) \frac{\partial \phi_1(\mathbf{r}_1)}{\partial r_1} \frac{\vec{r}_{13}}{r_{13}} \frac{\vec{r}_1}{r_1} d\tau_1 + \dots = \\ \int r_{12} \phi'_1(\mathbf{r}_1) \frac{\partial \phi_1(\mathbf{r}_1)}{\partial r_1} \frac{r_{13}^2 + r_1^2 - r_3^2}{2r_1 r_3} d\tau_1 + \dots & \quad (\text{A.32}) \end{aligned}$$

The term corresponding to the variable θ_1 :

$$\begin{aligned}
(\nabla_1^* \phi_1^*(\mathbf{r}_1)) (\nabla_1 r_{12}) = \\
\left(\frac{\partial \theta_1}{\partial x_1} \vec{i} + \frac{\partial \theta_1}{\partial y_1} \vec{j} + \frac{\partial \theta_1}{\partial z_1} \vec{k} \right) \left(\frac{\partial r_{12}}{\partial x_1} \vec{i} + \frac{\partial r_{12}}{\partial y_1} \vec{j} + \frac{\partial r_{12}}{\partial z_1} \vec{k} \right) \frac{\partial \phi_1(\mathbf{r}_1)}{\partial \theta_1} = \\
\left(\frac{\partial \theta_1}{\partial x_1} \frac{\partial r_{12}}{\partial x_1} + \frac{\partial \theta_1}{\partial y_1} \frac{\partial r_{12}}{\partial y_1} + \frac{\partial \theta_1}{\partial z_1} \frac{\partial r_{12}}{\partial z_1} \right) \frac{\partial \phi_1(\mathbf{r}_1)}{\partial \theta_1}
\end{aligned}$$

This expression can be transformed into polar and interelectronic coordinates, as shown in Ref. [15], with:

$$\cos(\theta_1) = \frac{z_1}{\sqrt{x_1^2 + y_1^2 + z_1^2}} \quad (\text{A.33})$$

$$\begin{aligned}
\frac{\partial \theta_1}{\partial x_1} &= \frac{z_1 x_1}{r_1^3 \sin \theta_1} \\
\frac{\partial \theta_1}{\partial y_1} &= \frac{z_1 y_1}{r_1^3 \sin \theta_1} \\
\frac{\partial \theta_1}{\partial z_1} &= \frac{z_1^2}{r_1^3 \sin \theta_1} - \frac{1}{r_1 \sin \theta_1}
\end{aligned} \quad (\text{A.34})$$

the coordinates are transformed as Ref. [15]:

$$\frac{\partial \theta_1}{\partial x_1} \frac{\partial r_{12}}{\partial x_1} + \frac{\partial \theta_1}{\partial y_1} \frac{\partial r_{12}}{\partial y_1} + \frac{\partial \theta_1}{\partial z_1} \frac{\partial r_{12}}{\partial z_1} = \frac{r_2}{r_1 r_{12}} \frac{\cos \theta_1}{\sin \theta_1} + \frac{1}{2} \cot \theta_1 \frac{r_{12}^2 + r_1^2 - r_2^2}{2 r_1 r_2} \quad (\text{A.35})$$

Finally

$$\left(\frac{\partial \theta_1}{\partial x_1} \frac{\partial r_{12}}{\partial x_1} + \frac{\partial \theta_1}{\partial y_1} \frac{\partial r_{12}}{\partial y_1} + \frac{\partial \theta_1}{\partial z_1} \frac{\partial r_{12}}{\partial z_1} \right) \frac{\partial \phi_1(\mathbf{r}_1)}{\partial \theta_1} = \left(\frac{r_2}{r_1 r_{12}} \frac{\cos \theta_1}{\sin \theta_1} + \frac{1}{2} \cot \theta_1 \frac{r_{12}^2 + r_1^2 - r_2^2}{2 r_1 r_2} \right) \frac{\partial \phi_1(\mathbf{r}_1)}{\partial \theta_1} \quad (\text{A.36})$$

The term in ϕ :

$$\tan \phi_1 = \frac{y_1}{x_1} \quad (\text{A.37})$$

$$\begin{aligned}
(\nabla_1^* \phi_1^*(\mathbf{r}_1)) (\nabla_1 r_{12}) = \\
\left(\frac{\partial \phi_1}{\partial x_1} \vec{i} + \frac{\partial \phi_1}{\partial y_1} \vec{j} + \frac{\partial \phi_1}{\partial z_1} \vec{k} \right) \left(\frac{\partial r_{12}}{\partial x_1} \vec{i} + \frac{\partial r_{12}}{\partial y_1} \vec{j} + \frac{\partial r_{12}}{\partial z_1} \vec{k} \right) \frac{\partial \phi_1(\mathbf{r}_1)}{\partial \theta_1} = \\
\left(\frac{\partial \phi_1}{\partial x_1} \frac{\partial r_{12}}{\partial x_1} + \frac{\partial \phi_1}{\partial y_1} \frac{\partial r_{12}}{\partial y_1} + \frac{\partial \phi_1}{\partial z_1} \frac{\partial r_{12}}{\partial z_1} \right) \frac{\partial \phi_1(\mathbf{r}_1)}{\partial \theta_1} \quad (\text{A.38})
\end{aligned}$$

$$\begin{aligned}
\frac{\partial \phi_1}{\partial x_1} &= -\frac{y_1}{r_1^2 \sin^2 \theta} \\
\frac{\partial \phi_1}{\partial y_1} &= \frac{x_1}{r_1^2 \sin^2 \theta} \\
\frac{\partial \phi_1}{\partial z_1} &= 0 \quad (\text{A.39})
\end{aligned}$$

$$\left(\frac{\partial \phi_1}{\partial x_1} \frac{\partial r_{12}}{\partial x_1} + \frac{\partial \phi_1}{\partial y_1} \frac{\partial r_{12}}{\partial y_1} + \frac{\partial \phi_1}{\partial z_1} \frac{\partial r_{12}}{\partial z_1} \right) \frac{\partial \phi_1(\mathbf{r}_1)}{\partial \theta_1} = \frac{r_2}{r_1 r_{12} \sin \theta_1} \sin(\phi_1 - \phi_2) \frac{\partial \phi_1(\mathbf{r}_1)}{\partial \phi_1} \quad (\text{A.40})$$

The obtained expressions Eqs. (51,55) agree with the Eqs. (64-66) which had to be evaluated in Ref. [14]. The solution of the Eqs. (51,55) requests the use of the derivatives over spherical harmonics and recursion relations of cosine and sinus functions and spherical harmonics, as already done in Ref. [14].

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Figure 1: Definition and rotation of the coordinates of two electrons in an atomic center.

